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Supporting Information

Heterogeneous hydroformylation of long-chain alkenes in IL-in-oil Pickering emulsion

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Characterization of water contact angles of solid materials

The sample tablets were prepared according to the method mentioned in literature ^{S1}. After drying at 100 °C in oven overnight, the silica nanospheres were pressed into tablets using a cylindrical stainless steel die of 1 cm in diameter under 10 MPa for 2 min. Water contact angle measurements were performed on KRÜSS DSA100 using water as testing liquid.



Fig. S1 TEM images of (a) DMSN-C18N-0.5, (b) DMSN-C18N-1.2 and (c) MCM-C18N-1.8.



Fig. S2 Nitrogen adsorption-desorption isotherms of DMSN-C18N-X (X=0.5, 1.2).



Fig. S3 CLSM images of emulsion formed with (a) DMSN-C18N-0.5 and (b) DMSN-C18N-1.2 by dying [BMIM][BF₄] with rhodamine 6G (scale bar, 100 μm).



Fig. S4 Photographs and microscopic images of emulsion systems with DMSN-C18N-X and MCM-C18N-1.8. Emulsion formation: 60 mg silica nanospheres, 1 mL of H₂O (including Rh 3.0 ×10⁻³ mmol, P/Rh=15) and 1 mL of 1-dodecene. The emulsions were kept under static conditions for different time intervals (scale bar, 200 μ m). (a) newly formed, (b) after 1 day, (c) after 3 days, (d) after 10 day.



Fig. S5 The photographs of IL-in-oil emulsion with DMSN-C18N-0.8 including different amount of tridecyl aldehyde (scale bar 200 μ m). Emulsion formation: 60 mg of silica nanospheres, 1 mL of [BMIM][BF₄] (including Rh 4.5 ×10⁻³ mmol, P/Rh=15) and 1 mL of oil phase including desired amount of 1-dodecene and tridecyl aldehyde with molar ratio of (a) 1:0 (conversion of 0%), (b) 4:1 (conversion of 20%), (c) 3:2 (conversion of 40%), (d) 2:3 (conversion of 60%), (e) 1:4 (conversion of 80%). The emulsions were kept under static conditions for 10 minutes.



Fig. S6 Photographs and microscopic images of the Pickering emulsion formed with reused DMSN-C18N-0.8 at the beginning of each reaction cycle (scale bar, 200 μ m).

Table S1 Comparison of the activity of hydroformylation of long chain alkenes with

System	Substrate	S/C	T (h)	Temp. (°C)	Conv. (%)	Sel. (%)	n/b	TOF (h ⁻¹)	Ref.
Oil-[BMIM[PF ₆] biphase	1-octene	1000	24	120	86	85	90:10	36	S2
Water-oil biphase	1-octene	3820	24	120	/	97	99:1	5	S3
Water-oil biphase	1-hexene	3000	48	120	13	100	97:3	24	S4
Water-oil microemulsion	1-dodecene	/	3	110	34	95	98:2	642	S5
Water-oil Pickering emulsion (cyclodextrin as emulsifier)	1-octene	508	24	120	90	99	95:5	/	S6

Rh-Sulfoxantphos as catalyst in biphase and emulsion systems

References

- S1 L. Forny, K. Saleh, R. Denoyel and I. Pezron, Langmuir, 2010, 26, 2333.
- S2 J. Dupont, S. M. Silva and R. F. de Souza, Catal. Lett., 2001, 77, 131.
- S3 M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer and P. W. N. M.van Leeuwen, J. Am. Chem. Soc., 2000, 122, 1650.
- S4 M. S. Goedheijt, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Mol. Catal.A-Chem.*, 1998, **134**, 243.
- S5 T. Hamerla, A. Rost, Y. Kasaka and R. Schomacker, *ChemCatChem*, 2013, **5**, 1854.
- S6 L. Leclercq, F. Hapiot, S. Tilloy, K. Ramkisoensing, J. N. H.Reek, P. W. N. M. van Leeuwen and E. Monflier, *Organometallics*, 2005, **24**, 2070.